



Anomalous Increase in Nematic-Isotropic Transition Temperature in Dimer Molecules Induced by a Magnetic Field

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We have determined the nematic-isotropic transition temperature as a function of an applied magnetic field in three different thermotropic liquid crystalline dimers. These molecules are comprised of two rigid calamitic moieties joined end to end by flexible spacers with odd numbers of methylene groups. They show an unprecedented magnetic field enhancement of nematic order in that the transition temperature is increased by up to 15 K when subjected to a 22 T magnetic field. The increase is conjectured to be caused by a magnetic-field-induced decrease of the average bend angle in the aliphatic spacers connecting the rigid mesogenic units of the dimers.

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Nematic liquid crystals (NLCs) are anisotropic fluids that only exhibit uniaxial, apolar orientational order. In most liquid crystals, this order is temperature dependent, spontaneously arising at temperatures below the nematic-isotropic ($N-I$) phase transition temperature (T_{N-I}); above this temperature the material exhibits no order (i.e., is isotropic). In many nematics, orientational order is particularly responsive to external influences, for example, electric and/or magnetic fields, mechanical strains, etc. [1–7]. This response is the primary reason that nematic liquid crystals are extensively used in information display applications like liquid crystal displays. External fields affect NLCs in two ways: they affect the degree of orientation order, or they reorient the axis of orientational order (the “director,” represented by a unit vector field \hat{n}).

The former effect was demonstrated with an electric field by Helfrich [8], who observed an increase in T_{N-I} when a large electric field was applied to a NLC. This increase scaled with E^2 , as was expected (see the discussion below); however, it did not exceed 1 °C, even at the largest electric fields used. This result has since been confirmed for numerous other materials. Indeed, mean-field theories of the $N-I$ transition predict a critical field at which the transition becomes continuous; this has also been observed for electric fields [9]. Lyotropic liquid crystal materials, in which solute concentration is more important than temperature in determining phase behavior, also exhibit field-enhanced order [10].

Magnetic field effects on orientational order are more difficult to observe because the diamagnetic anisotropy is effectively smaller than the dielectric anisotropy. In calamitic (rod-shaped) liquid crystals, applying a 10 T magnetic field only increases T_{N-I} by a few mK [11]. In these materials, the critical magnetic field is estimated to exceed

100 T. More recent work examining NLCs composed of less linear and reduced symmetry molecules, such as bent-core molecules, revealed larger (on the order of 1 K) shifts in T_{N-I} [12,13]. Neither of these results is explicable within the context of classical mean-field theories for the $N-I$ transition, such as Landau–de Gennes or Maier-Saupe theories. Instead, the large shift was attributed to additional degrees of freedom: for example, the presence of local polar order or fluctuations of positional order. A detailed calculation of the effects of molecular biaxiality found that this may also lead to anomalously large field effects for the $N-I$ transition [14].

In this work, we report on unprecedented magnetic-field-induced shifts of the isotropic-nematic ($I-N$) phase transition temperature observed in liquid crystal dimers where two rigid linear mesogens are linked by flexible nonyl or heptyl chains [15]. The shapes of these molecules resemble *nunchaku* fighting sticks. The three compounds studied and their corresponding phase sequences are depicted in Fig. 1(a). The first compound, 1'',7''-bis(4-cyanobiphenyl-4'-yl)nonane (CB9CB), was synthesized as described in Ref. [16]. The synthesis of the second and third dimers, 1,1,1-di(2',3''-difluoro-4-pentyl[1,1';4',1'']terphen-1''-yl)nonane (DTC5C9) and 1,1,1-di(2',3''-difluoro-4-pentyl[1,1';4',1'']terphen-1''-yl)heptane (DTC5C7), is described in Ref. [17]. The three compounds exhibit the recently discovered twist-bend nematic (N_{TB}) liquid crystal phase, in which the director follows an ambidextrous conical helix with a remarkably short pitch in the 10 nm range [18,19]. Thus, the N_{TB} phase can be considered as a nanoscale pseudolayered structure [20–22], which explains the smectic-like textures [20–24] and viscoelastic properties [25] of the N_{TB} phase, despite the lack of a density modulation characteristic of a true smectic [18,24,26].

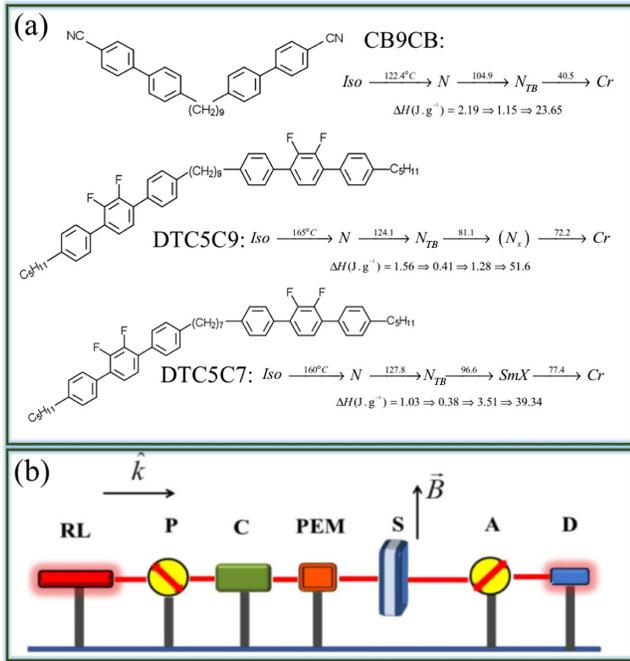


FIG. 1. Materials studied and experimental setup. (a) Chemical structures, abbreviated names, and phase sequences of the mesogens investigated. (b) Experimental setup. RL: 30 mW, $\lambda = 632.8$ nm He-Ne laser; S: LC sample placed between crossed polarizers (P and A) oriented at $\pm 45^\circ$ with respect to the vertical magnetic field; C: compensator to correct for residual birefringence; PEM: photoelastic modulator; D: photodetector positioned to measure the direct transmitted beam. Using this arrangement, the protocol is to either measure the effective birefringence as a function of an applied field at fixed temperature, or the effective birefringence as a function of temperature at a fixed field.

In our experiments we load each compound in a 10×10 mm planar glass cell whose inner surfaces are treated with a unidirectional rubbed polyimide PI2555 (HD Micro Systems) that promotes molecular alignment parallel to the substrates (homogeneous planar alignment) and along the rubbing direction; the distance d between substrates was $5 \mu\text{m}$. The filled liquid crystal cell is then inserted into a Teflon-insulated temperature-controlled oven (temperature stability $\pm 0.05^\circ\text{C}$) with optical access. Two high-precision temperature sensor probes are embedded in the oven; one is a glass-encapsulated thermistor and the other a platinum resistance thermometer. Neither showed any drift during application of high magnetic fields. The oven is inserted into the bore of the 25 T split-helix resistive solenoid magnet at the National High Magnetic Field Laboratory [27]. This magnet has ports allowing optical access perpendicular to the field direction. The oven and the liquid crystal cell inside are oriented so that the optical path is orthogonal to the field. The rubbing direction of the planar cell (optic axis) is parallel to the field. A standard optical setup [Fig. 1(b)], incorporating photoelastic modulator and lock-in amplifiers, was used to measure field-induced changes in optical birefringence [28]. This setup

records the phase difference between ordinary and extraordinary rays, $\varphi = 2\pi\Delta n d/\lambda$, where Δn is the effective birefringence of the sample [28–30] and λ is the wavelength of light (632.8 nm).

The temperature dependencies (on cooling) of the effective birefringence Δn and the dependence of T_{N-I} on magnetic fields are shown in Fig. 2. At the zero field, the discontinuity in birefringence at T_{N-I} is plainly visible in CB9CB; it is smaller for the two other compounds. Under magnetic fields the birefringence is larger in the entire nematic range, although the increment at the $N-I$ transition appears smoother. The field-induced increase of the birefringence may indicate quenching of the fluctuations and/or an increased aspect ratio of the molecules. The data shown correspond to cooling from above T_{N-I} . The same behavior is observed in heating, although the transition temperature is observed to be approximately 1°C higher.

In a 22 T magnetic field, T_{N-I} increases dramatically, by at least 8°C in all three compounds and by almost 15°C for DTC5C7. We know of no other example of such a large magnetic field effect on a nematic-isotropic transition for a thermotropic liquid crystal. Indeed, this effect is more than 300 times larger than what has been reported previously for rod-shaped thermotropic compounds. We also performed measurements at several weaker magnetic fields. As can be seen on the right-hand side of Fig. 2, the transition temperature shift ΔT_{N-I} increases almost proportionally to B , and is not proportional to B^2 , as was found for other thermotropic materials [11,13].

When the samples are held at temperatures just above the zero-field T_{N-I} and are then subjected to an increasing magnetic field, the field induces the nematic phase. If the field is subsequently reduced to 0, the isotropic phase returns to a field just slightly lower than that at which the nematic phase was induced. No discontinuity in birefringence (as in Fig. 2) is observed in this field-induced transition (see Fig. 3), due to the fact that the field was continuously changing (typically at 5 T/min) during the measurements. At temperatures further away from the zero-field T_{N-I} the threshold field where the $I-N$ transition is induced increases, as seen in Figs. 3(a)–(3c). In Fig. 3(d) we compare $\Delta n(B)$ of the three studied materials at 5 K above the zero-field T_{N-I} . The compound CB9CB shows a more rapid onset of birefringence with an applied magnetic field compared to the other compounds.

Magnetic fields interact with liquid crystals mainly via the molecules' aromatic ring moieties. The free energy contribution due to an applied field is minimized when the ring plane normals are perpendicular to the field. In fully rigid molecules this occurs with the molecular long axis aligning parallel to the field. The most profound effect of this interaction is the reorientation of rigid rod-shaped molecules along the external field. Additionally, when the director is already aligned along the field, a magnetic field can couple to the magnitude of the orientational order, which can be described by Landau-de Gennes [31] or Maier-Saupe [32] theories. Both theories predict that a magnetic field leads

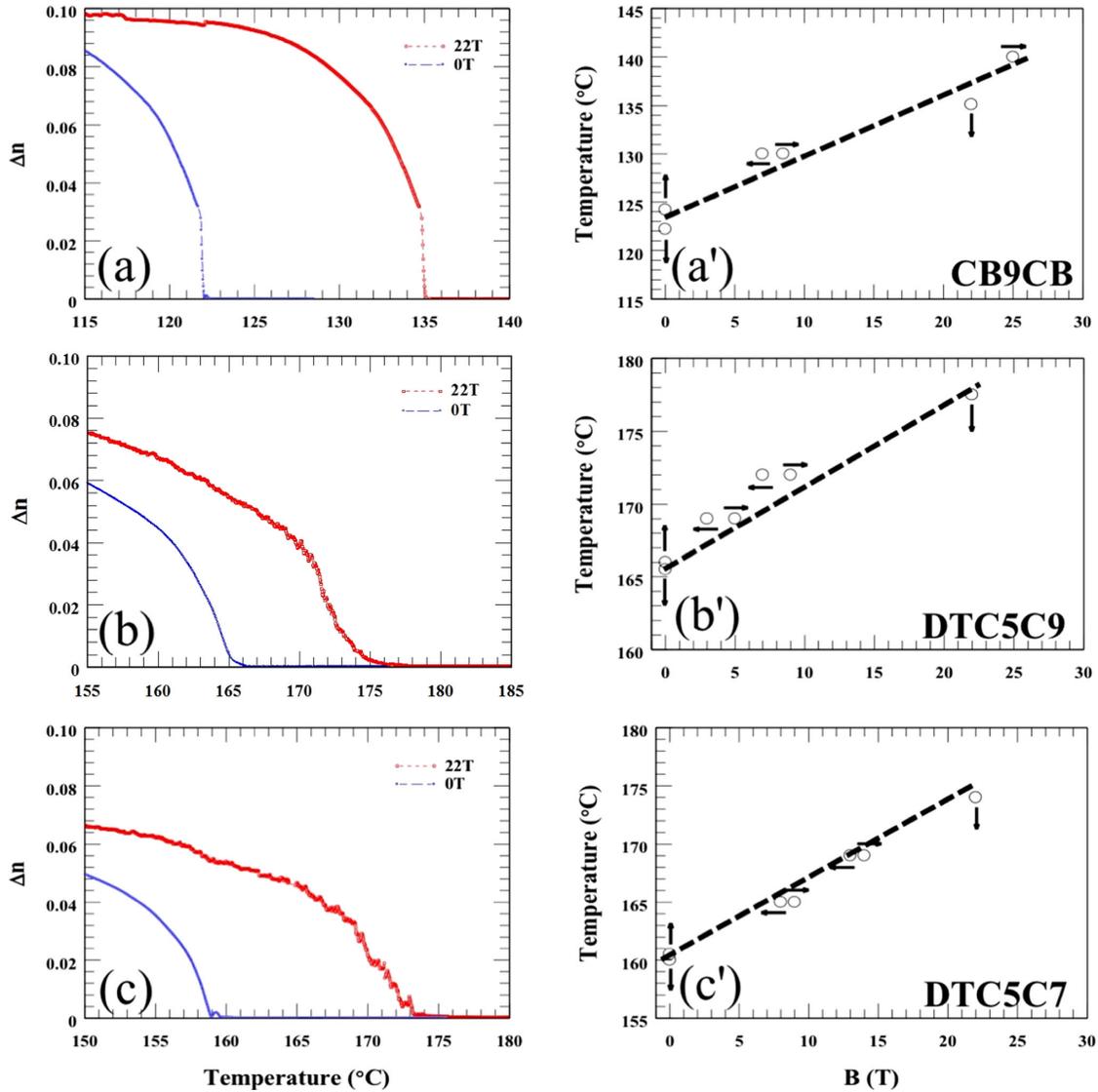


FIG. 2. Temperature dependence of effective birefringence and magnetic field dependence of the $I - N$ transition temperatures. Left: Temperature dependence of birefringence at $B = 0$ (blue) and $B = 22$ T (red) for CB9CB (a), DTC5C9 (b), and DTC5C7 (c) measured on cooling at a $2^\circ\text{C}/\text{min}$ rate. Right: T_{N-I} as a function of the magnetic field B for CB9CB (a'), DTC5C9 (b'), and DTC5C7 (c'). Data with arrows up arrow, down arrow, right arrow, left arrow are taken on heating, cooling, increasing fields, and decreasing fields, respectively.

induces a ΔT_{N-I} that is linear in $\Delta\chi_0$, quadratic in B in contrast to our observations shown in Figs. 2(a')–2(c'). They show that in our dimers the $N - I$ transition temperature increases roughly linearly with the magnetic field. A possible linear contribution to the phase shift related to field-induced quenching has been discussed by Dhara and Madhusudana [33]. However, this effect is even smaller than the field-enhanced order that is contained in Landau–de Gennes theory and as such is not a candidate for explaining the linear dependence we observe.

Moreover, Landau and de Gennes predict that T_{N-I} also depends inversely on the latent heat of the $N - I$ transition. However, in order for this mechanism to explain the magnitude of ΔT_{N-I} observed, these compounds would require either (i) diamagnetic anisotropy hundreds of times

larger than in typical rod-shaped thermotropic compounds (which may be ruled out due to their similar cores based upon aromatic rings) or (ii) $N - I$ latent heat thousands of times smaller, which is also not the case [34].

Hence we conclude that field enhancement of nematic order, as predicted by the Landau–de Gennes theory for simple rodlike mesogens, cannot explain the observed values for ΔT_{N-I} . Lastly, the three compounds we have studied show no indications of other varieties of ordering (or fluctuations thereof), such as positional clustering [17,23,25] or biaxiality, which have been proposed to explain otherwise inexplicably large ΔT_{N-I} [12,13].

Most theories relating molecular morphology to the onset of the $N - I$ transition derive from Onsager [35]; however, approaches based only on excluded volume

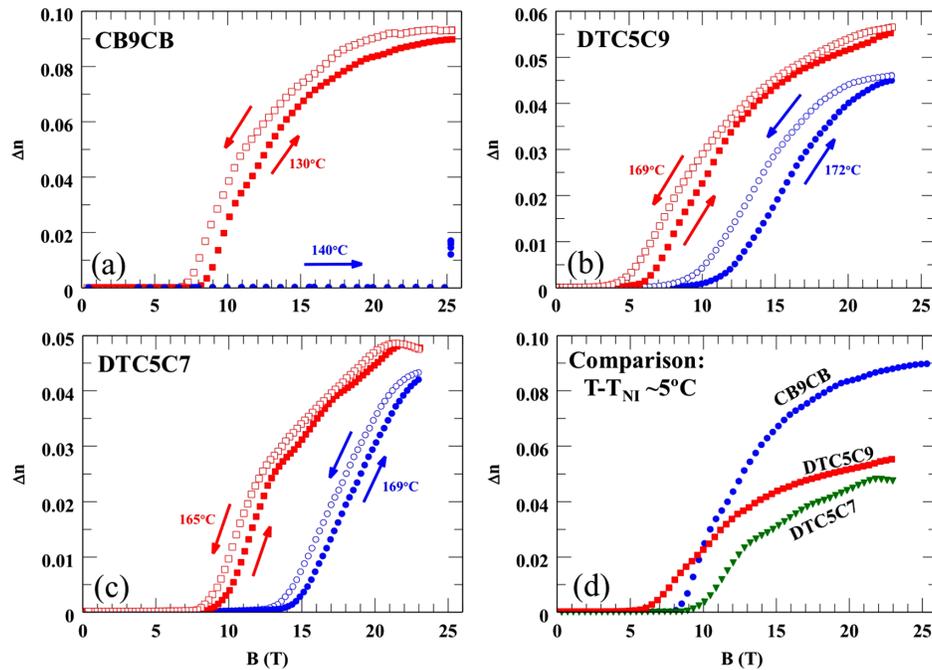


FIG. 3. Effective birefringence measurements as the function of magnetic field B : (a) CB9CB at 130 and 140 °C; (b) DTC5C9 at 169 and 172 °C; and (c) DTC5C7 at 165 and 169 °C. The arrows \uparrow (\downarrow) show measurements at the field ramping up (down) at a 5 °C/ min rate. (d) Comparison of the three materials at 5 °C above the zero-field T_{N-I} .

effects are athermal and cannot provide insight to transition temperatures. Onsager-type models have been hybridized [36,37] to contain the effects of both anisotropic, rigid shapes and anisotropic inter-molecular interactions (treated via the mean field). While these models do not aspire to describe the more complex shaped mesogens in the present work, they do indicate that T_{N-I} increases strongly with mesogens' aspect ratio (length/diameter). This fits broadly with experimental results for linear rigid aromatic ring systems [36–38].

Owing to the odd-numbered methylene groups in the linking group, the average molecular shape of the materials we studied is bent (i.e., nonzero β_0 as shown in Fig. 4). However, due to the inherent flexibility of the alkyl bridge between the two arms, the shape can be relatively easily altered. A decrease of the bend angle effectively increases the aspect ratio of the dimer, which should produce a significant increase of T_{N-I} ; this is predicted by multiple models [39–41]. For example, Ref. [39] estimates that, for dimers linked by a nonyl chain, a reduction of only 3° leads to a 4% increase in T_{N-I} (in absolute temperature), which is larger than the shift we report. This suggests that a magnetic-field-induced straightening of the molecules is responsible for the magnetically induced large shift of T_{N-I} recorded in our experiments in high fields. The role of the molecular shape on T_{N-I} is also evidenced in the anomalously large “odd-even” effects observed in the T_{N-I} transition temperature. For an even number of methylene linkages (that promote a straight or linear molecular conformation) the phase transition temperatures for % 1",7"-bis (4-cyanobiphenyl-4'-yl)alkane % (CBnCB) molecules were found to be

50 °C higher than for the odd-numbered homologs that possess a more bent shape [42,43].

Our hypothesis is therefore that the effect of a large field is that it straightens out the dimers on average, aligning the two rigid arms more parallel to a common axis than would be found in the zero field. This mechanism is illustrated in Fig. 4. We note that the effect of the shape, i.e., the odd-even effect, is

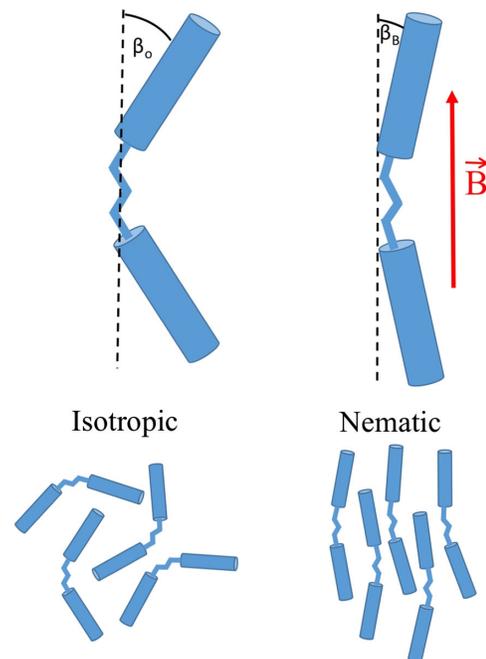


FIG. 4. Illustration of the magnetic-field-induced decrease of the molecular bend, and its consequence of the shift of T_{N-I} .

decreasing toward higher homologs, which is corroborated by our observation (see Fig. 2) that the field-induced phase shift is smaller for DTC5C9 than for DTC5C7.

Here, we note that the magnetic-field-induced downward shift of the $N - N_{TB}$ transition of two other dimers CB7CB and KA(0.2) has already been reported by Challa *et al.* [30]. This seems to confirm our conjecture about the straightening of the dimers, although the theory by Vanakaras and Photinos [41] allows both positive and negative $\Delta T_{N-N_{TB}}$. Studies of magnetic-field-induced $I - N$ and $N - N_{TB}$ phase transition shifts on a large number of dimers are in progress.

To summarize, we have observed a large magnetic-field-induced elevation in the nematic to isotropic phase transition temperature in various thermotropic liquid crystal dimers containing an odd number of methylene groups in the linkage between the two terminal mesogenic moieties. We attribute this unprecedented shift to a field-induced straightening in the average conformation of the dimers. The impact of an electromagnetic field at the molecular level on the ordering of an ensemble of mesogens has not (to our knowledge) been previously reported.

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